



Cs exchanged phosphotungstic acid as an efficient catalyst for liquid-phase Beckmann rearrangement of oximes

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ABSTRACT

Cs exchanged phosphotungstic acid is a highly efficient and environmentally benign solid acid catalyst for the liquid-phase Beckmann rearrangement of ketoximes to the corresponding amides. The catalysts $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($x = 1.5, 2, 2.5$ and 3) were prepared by a titration method. The characterization results indicated that the primary Keggin structure remained intact after exchanging the protons with Cs ions. Moreover, the Cs exchanged catalysts were insoluble and exhibited larger BET surface area than the parent acid. The catalysts exhibited high reactivity and selectivity for the formation of ϵ -caprolactam, the precursor of Nylon 6, from cyclohexanone oxime. The catalyst can be recovered after reaction without any structural transformation.

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1. Introduction

The transformation of ketoximes to amides, known as the Beckmann rearrangement, has been extensively studied recently. The most important industrial example is the production of ϵ -caprolactam, which is the precursor of Nylon 6, from cyclohexanone oxime (Scheme 1). This commercial process involves a liquid phase rearrangement using fuming sulfuric acid as both catalyst and reaction medium [1]. A large amount of ammonium sulfate is produced during the neutralization of sulfuric acid to release the ϵ -caprolactam. Great efforts have been put into the development of a clean Beckmann rearrangement process that avoids the use of concentrated sulfuric acid, the corresponding problem of corrosion and the formation of ammonium sulfate byproduct. A number of solid acid catalysts such as zeolites, MCM-41, silica, alumina, silica–alumina and supported metal oxides have been investigated for the vapor-phase rearrangement of cyclohexanone oxime in order to replace the environmentally unfriendly process using sulfuric acid [2–33]. However, the vapor-phase reactions require higher temperatures, usually above 573 K, to keep the oxime and products in the vapor-phase. It is desirable to conduct the reaction under relatively mild liquid phase conditions, which may be preferred energetically.

Recently heteropoly acids (HPAs) have received attention as acid and oxidation catalysts for many reactions and have been introduced in some industrial processes such as hydrations of *n*-butene and isobutylene, polymerization of tetrahydrofuran, synthesis of acetic acid from ethylene, etc [34–36]. They are characterized by strong acidity. However, because of their low surface area, the amount of acid sites on the surface is small. The surface area and pore structure can be increased by the substitution of protons by alkali cations. The salts with large monovalent ions such as Cs^+ are insoluble and possess high surface areas. It has been observed that the Cs salt is more active than the parent acid form for a number of reactions including alkylations, acylations, direct decomposition of esters, isomerization of *n*-butane, hydration of olefins, hydrolysis of esters in excess water, and biodiesel synthesis [37–49]. It was found that Beckmann rearrangement of cyclododecanone oxime on $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ in solid–solid reaction system at 373 K gave 24.3% yield to the corresponding lactam [50].

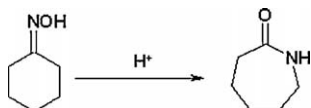
In this study, we show that Cs exchanged $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is an efficient and environmentally benign catalyst for liquid phase Beckmann rearrangement of oximes to the corresponding amides or lactams. We have investigated the rearrangement of a number of oximes, however, the main emphasis in this paper is on the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam in the liquid phase (Scheme 1).

2. Experimental

Cs salts of phosphotungstic acid, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($x = 1.5, 2, 2.5, 3.0$), were prepared by a titration method following a reported

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Scheme 1. Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam.

procedure [48]. An appropriate amount of aqueous solution of Cs_2CO_3 (Aldrich) was added dropwise with a constant rate to an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (20 cm^3 , Sigma–Aldrich) at room temperature with vigorous stirring. The Cs content was adjusted through the amount of Cs_2CO_3 solution added. After aging at room temperature overnight, the water was slowly removed by evaporation at 323 K . The zeolite samples were obtained from Catal International, Sheffield, U.K. and SAC-13 from Aldrich. Prior to the reaction, the catalysts were dried at 423 K for 12 h .

Cyclohexanone oxime was obtained from Sigma–Aldrich, UK and other oximes were synthesized from the corresponding ketones by reaction with hydroxylamine hydrochloride in a mixture of ethanol and pyridine at 358 K , by the general method reported in the literature [51]. The oximes were purified by recrystallization with ethanol. The rearrangements of oximes were carried out in the liquid phase at 353 – 423 K in a 50 ml glass reactor equipped with a condenser and a magnetic stirrer. Tetradecane (Koch–Light Laboratories, UK) was added as a GC internal standard. To monitor the reaction, 0.1 ml samples of the reaction mixture were taken periodically and analysed by gas chromatography (PerkinElmer Clarus 500) using a 50 m BP1 capillary column and an FID detector. The N_2 adsorption–desorption isotherms were measured at 77 K on a Micromeritics ASAP-2000 after evacuation at 473 K for 5 h . The surface area and the pore size distribution curve were calculated by the BET and BJH (mesopore), Horvath–Kawazoe (micropore) method, respectively. Powder X-ray diffraction patterns were collected on a Bruker diffractometer using $\text{Cu K}\alpha$ radiation. FTIR spectra were collected on a Nicolet 800 (ThermoFinnigan corporation) spectrometer. The system used for ammonia adsorption flow calorimetry has been described previously [52,53]. It is based on a Setaram 111 DSC with an automated gas flow and switching system, with a mass spectrometer (Hiden HPR20) to sample the downstream gas flow. The sample (20 – 30 mg) was held on a glass frit in a vertical silica sample tube and activated at 150°C under a dried helium flow (5 ml min^{-1}) for 5 h . After activation, the sample temperature was maintained at 150°C and 1 ml pulses of the probe gas (1% ammonia in helium) at atmospheric pressure were injected at regular intervals into the carrier gas stream from a gas sampling valve. The ammonia concentration downstream of the sample was monitored continuously by mass spectroscopy. The pulse interval was chosen to ensure that the ammonia concentration in the carrier gas returned to zero to allow the DSC baseline to stabilise. The net amount of ammonia irreversibly adsorbed from each pulse was determined by comparing the MS signal with that recorded through a control experiment with a blank sample tube. The net heat released by each pulse was calculated from the thermal DSC curve.

3. Results and discussion

Cesium salts $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($x = 1.5, 2, 2.5, 3.0$), obtained as white powder in quantitative yield, are water stable and nonhygroscopic. Fig. 1 shows the powder XRD patterns of the dried Cs salts. The XRD patterns are in agreement with those reported in previous studies [41,48]. The salt Cs = 1.5 possesses some of the peaks exhibited by the parent phosphotungstic acid, as observed before. The intensities of those peaks decrease with the increase in Cs content. FTIR spectra of the samples are shown in

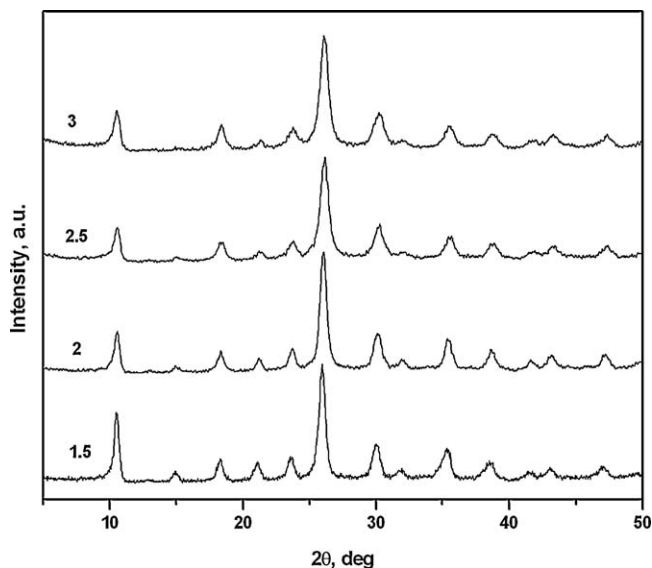


Fig. 1. Powder XRD patterns of Cs exchanged phosphotungstic acid catalysts. The numbers in the figure indicate the number of Cs ions exchanged.

Fig. 2. The IR spectra of all samples show the characteristic bands at ca. 1080 and 980 cm^{-1} assigned to the asymmetric stretching vibration of the P–O bond in the central PO_4 tetrahedron, and the stretching vibration of $\text{W}=\text{O}_t$ (terminal oxygen in the Keggin structure), respectively, which indicates the presence of the $\text{PW}_{12}\text{O}_{40}^{3-}$ anion after the exchange of protons in the parent acid by the Cs cations. The bands at 890 and 790 cm^{-1} correspond to the W–O–W (corner) and W–O–W (edge) vibrations, respectively (Fig. 2). The Keggin anion structure consists of a central PO_4 tetrahedron surrounded by 12 WO_6 octahedra, which form four W_3O_{13} groups [35,54]. The WO_6 octahedra share edges in W_3O_{13} groups and corners with other groups and with the central tetrahedron through bridging oxygens.

The surface area of $\text{Cs}_3\text{HPW}_{12}\text{O}_{40}$ sample was $134\text{ m}^2\text{ g}^{-1}$ while that of the parent $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{Cs}_{1.5}$ were $<10\text{ m}^2\text{ g}^{-1}$. $\text{Cs}_{1.5}$ and Cs_2 exhibited Type II isotherms, which are ordinarily observed for nonporous materials. For $\text{Cs}_{2.5}$ and Cs_3 , Type IV isotherms and hysteresis loop were observed, which are usually exhibited by mesoporous materials (Fig. 3). Nitrogen adsorption isotherm data

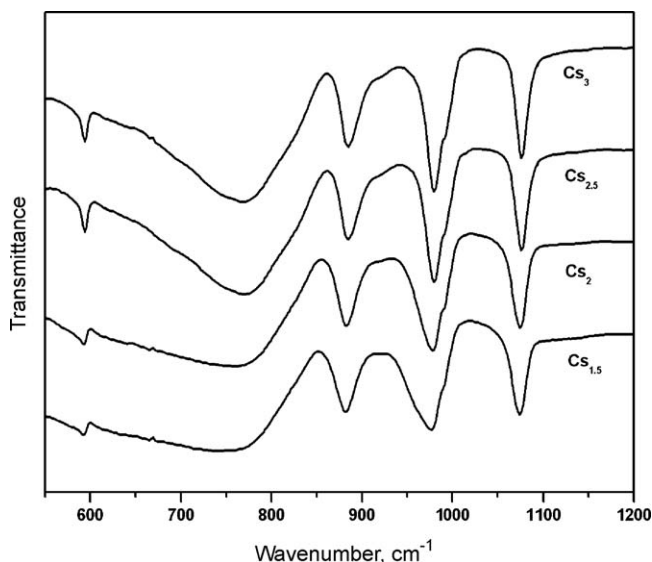


Fig. 2. FTIR spectra of Cs exchanged phosphotungstic acid catalysts.

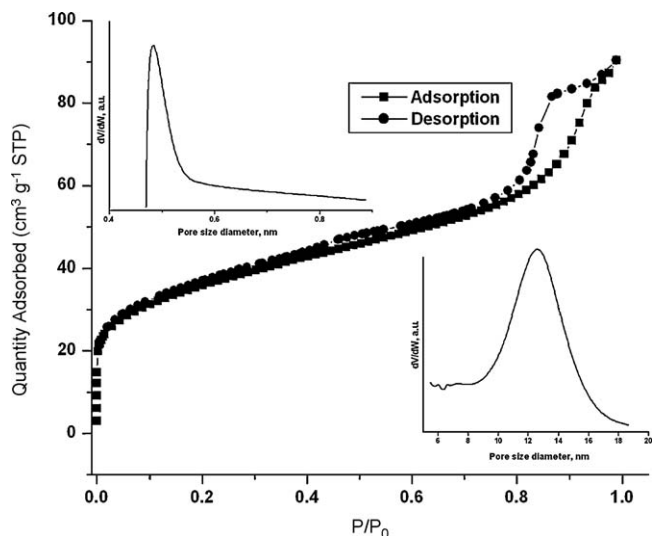


Fig. 3. N_2 adsorption isotherm and pore size distribution of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The micropore (inset, top) and mesopore (inset, bottom) sizes were estimated by Horvath-Kawazoe and BJH method, respectively.

also suggest the presence of micropores for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Fig. 3). The presence of micropores for NH_4^+ and Cs^+ salts has been observed before and was assigned to the pores present in the crystal structure of the salts [55].

The performances of Cs exchanged phosphotungstic acid catalysts in the liquid-phase Beckmann rearrangement of cyclohexanone oxime are shown in Fig. 4A and B. $Cs_{1.5}$, Cs_2 and $Cs_{2.5}$ are very active in converting cyclohexanone oxime to ϵ -caprolactam while Cs_3 is much less active. The low activity of Cs_3 is due to the exchange of all the protons of the parent phosphotungstic acid and correspondingly lower acidity, which is confirmed by the NH_3 adsorption microcalorimetry (Fig. 5). The initial heat of NH_3 sorption is about 140 kJ mol^{-1} for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ indicating strong acid sites for this sample while that of Cs_3 indicates negligible acidity. The oxime conversion increased with reaction time, with selectivity patterns being more or less similar. After 6 h of reaction, Cs salts ($x = 1.5, 2, 2.5$) exhibited ~60–70% conversion of cyclohexanone oxime at 403 K in benzonitrile solvent with highest selectivity to lactam for $Cs_{2.5}$ (Fig. 4). Cyclohexanone was observed as the byproduct, apparently formed by the hydrolysis of the oxime using traces of water remaining in the solvent. When strongly acidic catalysts are used in vapor-phase, selectivity for the desired ϵ -caprolactam is usually lower due to the formation of more byproducts. The heterogeneity of the reactions were verified by filtering off the catalyst from the reaction mixture after which reaction ceased. Negligible conversion of cyclohexanone oxime was observed when the reaction was conducted without any catalyst.

The conversion of oxime depends on the reaction temperature (Table 1). The conversion was ~42% at 353 K after 6 h using $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as catalyst and increased to 81% at 423 K. ϵ -Caprolactam is the major product at all temperatures, with selectivities around 90%. The catalytic performance of $Cs_{2.5}$ salt is compared with other solid acids in Table 1. The specific activity (number of moles of cyclohexanone oxime converted per unit area of the catalyst per unit time) of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is higher than that of a HY zeolite ($SiO_2/Al_2O_3 = 6$) while it was lower than resin-based SAC-13 (13% Nafion–silica composite) catalyst (Table 1). The difference in catalytic performances of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, HY and SAC-13 could be related to the difference in acidity of these samples. The Beckmann rearrangement is commonly believed to be initiated by protonation at the oxime group [56], hence these

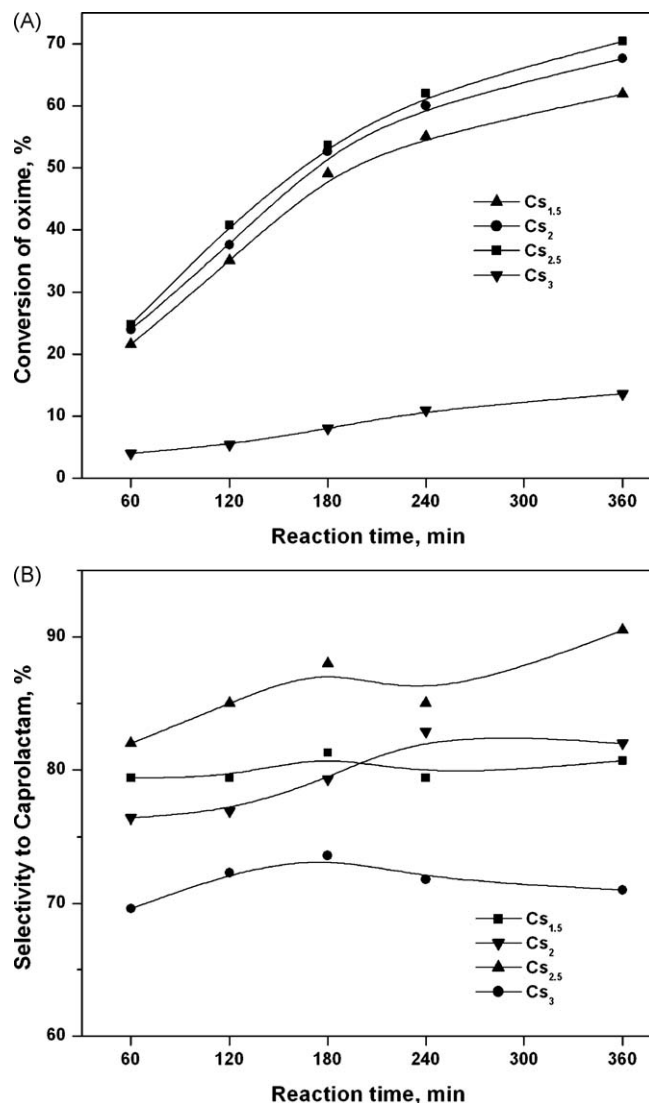


Fig. 4. Conversion of oxime (A) and selectivity to caprolactam (B) as a function of reaction time for Cs containing phosphotungstic acid with different Cs contents. Reaction conditions: catalyst, 0.1 g; oxime, 1 mmol; solvent, 10 ml benzonitrile; $T = 403 \text{ K}$.

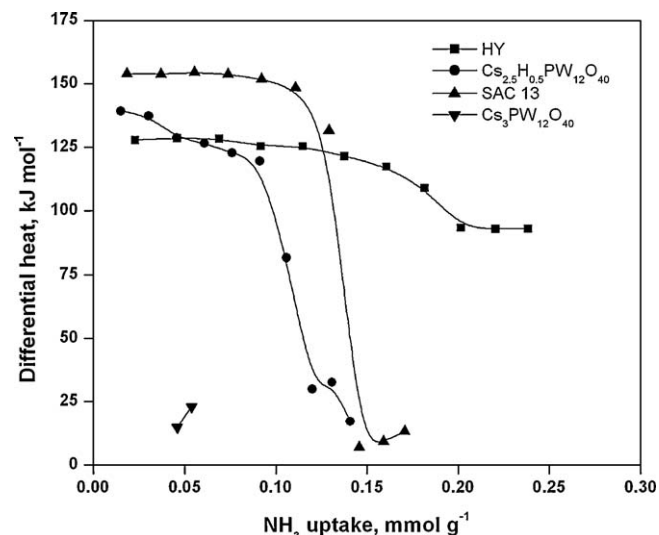


Fig. 5. Differential heat of ammonia adsorption on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_3PW_{12}O_{40}$, HY and SAC-13 catalysts.

Table 1Catalytic performance of Cs_{2.5}H_{0.5}PW₁₂O₄₀ and other catalysts in liquid-phase Beckmann rearrangement of cyclohexanone oxime.

Catalyst	T (K)	t (h)	Oxime Conv. (%)	ϵ -Caprolactam selectivity (%)	Specific activity ^a
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	353	6	42.3	85.4	12.3
	373	6	55.7	91.0	
	403	6	61.9	90.5	
		20	69.5	88.7	
		26	79.4	87.7	
	423	6	80.8	88.9	
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ Recycle 1	403	6	60.1	91.7	26 ^d
Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ Recycle 2	403	6	58.8	90.7	
SAC-13	403	6	27.3	85.7	
		20	51.5	87.1	
		26	56.5	85.8	
HY ^b	403	6	71.2	75.0	3.9
HZSM-5 ^c	403	6	22.2	56.8	10.4
		20	43.2	63.9	

^a 10^{−9} mol m^{−2} min^{−1}.^b SiO₂/Al₂O₃ = 6.^c SiO₂/Al₂O₃ = 27.^d Based on nafion content of SAC-13; solvent: benzonitrile; catalyst: 100 mg; oxime: 1 mmol.

results indicate Brønsted acidic strength of Cs_{2.5}H_{0.5}PW₁₂O₄₀ is intermediate between that of HY and SAC-13. This is also supported by the lower amount of cyclohexanone formed with Cs_{2.5}H_{0.5}PW₁₂O₄₀ compared to HY since weak Lewis acid sites are proposed to be responsible for cyclohexanone formation [22,27,28]. The heats of NH₃ adsorption measured by microcalorimetry support these observations (Fig. 5). Initial heats of NH₃ sorption were about 140, 150 and 128 kJ mol^{−1} for Cs_{2.5}H_{0.5}PW₁₂O₄₀, SAC-13 and HY, respectively. The average heat of NH₃ adsorption observed to decrease only slightly with Cs doping in a previous study also, suggesting that the residual acid strength of the partially Cs exchanged phosphotungstic acid materials is not strongly perturbed during proton exchange [49]. Hence, it can be concluded that the acid sites present on Cs_{2.5}H_{0.5}PW₁₂O₄₀ possess an appropriate strength, which are more suitable for catalyzing the Beckmann rearrangement of cyclohexanone oxime.

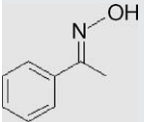
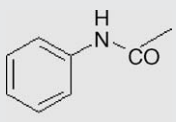
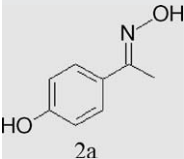
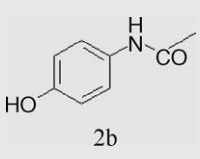
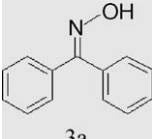
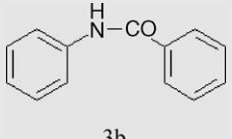
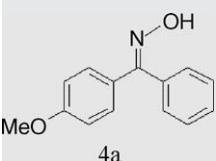
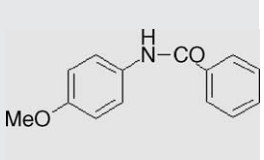
The Beckmann rearrangements of other oximes (see Table 2) have been investigated using Cs_{2.5}H_{0.5}PW₁₂O₄₀ to find the general applicability of these catalysts in converting oximes. As shown in Fig. 6, the catalyst is highly active in the rearrangement of different oximes such as acetophenone (1a), *p*-hydroxy acetophenone (2a), benzophenone (3a) and 4-methoxybenzophenone oximes (4a). Cs_{2.5}H_{0.5}PW₁₂O₄₀ is more active for the rearrangement of these oximes than that of cyclohexanone oxime and nearly complete conversions are observed at relatively short times with 100% selectivity to the desired rearranged product in all cases (Fig. 6). All these rearrangements are commercially important, and that of 4-hydroxy acetophenone oxime is of special interest because the rearranged product *N*-acetyl-*p*-aminophenol (acetaminophen or paracetamol, 2b) is a commonly used non-steroidal anti-inflammatory drug [31]. The conventional route of preparation of this drug involves acetylation of *p*-aminophenol with acetic anhydride. However, the conventional process has disadvantages such as the difficulty of mono acetylating the amine group and the possible oligomerization of the hydroxy aromatic amine. A different route was proposed by Davenport et al. for the preparation of *N*-acetyl-*p*-aminophenol involving the reaction of 4-hydroxyacetophenone with hydroxylamine hydrochloride to obtain the ketoxime (4-hydroxyacetophenone oxime), followed by the Beckmann rearrangement in the presence of an acid catalyst, such as mineral acids or ion-exchange resins in liquid sulfur dioxide [31,57]. Similar to the case of cyclohexanone oxime rearrangement, the use of solid

acid catalysts offers significant advantages over homogeneous acid catalysts, however, much less work has been reported in this case. The efficiency of MCM-41, ITQ-2, Beta, and MCM-22 were investigated for the rearrangement of 4-hydroxyacetophenone oxime to paracetamol previously [31,58], while this is the first report of the investigation of a heteropoly acid related catalyst for this purpose, to our knowledge.

The nature of solvent influences the reaction significantly. Table 3 shows the conversions of cyclohexanone oxime and product distributions over Cs_{2.5}H_{0.5}PW₁₂O₄₀ in various solvents

Table 2

Oximes studied and their products resulting from Beckmann rearrangement.

Oxime	Rearranged product
 1a	 1b
 2a	 2b
 3a	 3b
 4a	 4b

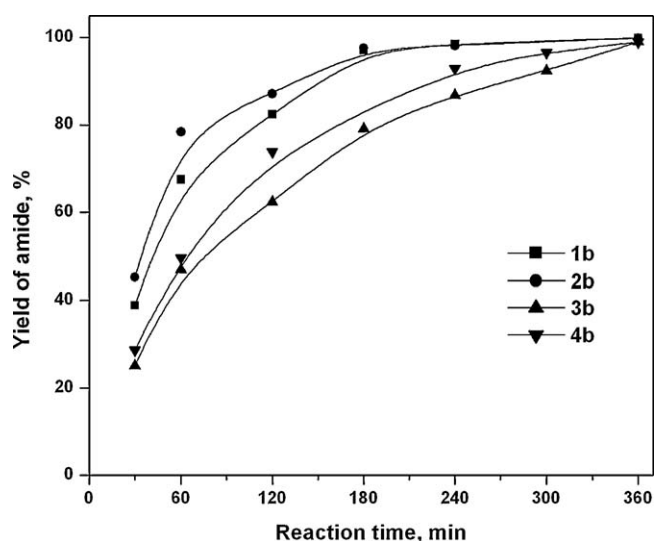


Fig. 6. Liquid phase rearrangement of various oximes; Solvent: benzonitrile; $T = 403$ K; oxime: 1 mol; catalyst: 100 mg. For the meaning of symbols, please refer Table 2.

Table 3

Effect of nature of solvent on the conversion and product distribution in Beckmann rearrangement of cyclohexanone oxime.

Solvent	Dielectric constant	Conv. (%)	^a S_{cl}	^b S_{ch}
Benzonitrile	25.2	61.9	90.5	9.5
DMSO	49.0	10.2	45.2	54.8
DMF	36.7	3.9	19.3	80.7
Chlorobenzene	5.6	8.6	15.4	84.6
Acetonitrile ^c	37.5	3.2	35.5	64.5

Reaction conditions: $T = 403$ K, $t = 6$ h, Solvent = 10 ml.

^a S_{cl} = selectivity to caprolactam.

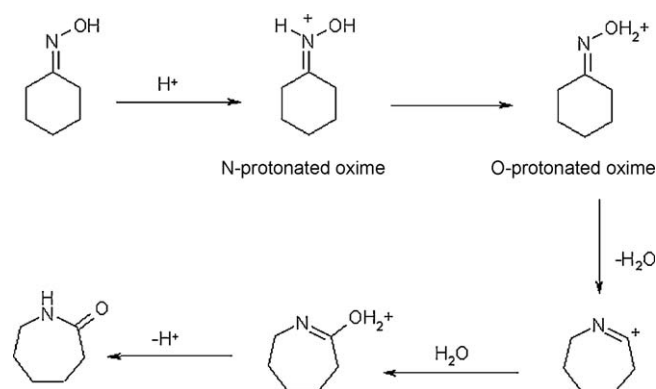
^b S_{ch} = selectivity to cyclohexanone.

^c Reaction temperature = 353 K.

with different polarities. Approximately equal selectivities to caprolactam and cyclohexanone at ~10% conversion of cyclohexanone oxime are observed in DMSO. The conversions of oxime were lower when the reactions were conducted in solvents such as DMF and chlorobenzene. The major product in these cases was cyclohexanone, formed by hydrolysis of cyclohexanone oxime and consequently the selectivity to the lactam was very low. Benzonitrile was found to be most suitable solvent since the activity and selectivity to the lactam were very high when the rearrangement was performed in benzonitrile. Moreover, the major product was ϵ -caprolactam and formation of cyclohexanone was negligible after prolonged reaction periods.

The catalytic performance of $Cs_{2.5}H_{0.5}PW_{12}O_4$ in chlorobenzene, which has a low dielectric constant, is also low (Table 3). Hence, it can be concluded that the dielectric constant of benzonitrile, which is intermediate between those of DMSO and chlorobenzene, is optimal for the facile desorption of lactam from catalyst. It shows that the polarity and basicity of the solvent are critical for the efficient rearrangement of oxime to the desired lactam, especially since the operating temperatures in the present experiments are much lower than those under the vapor-phase Beckmann rearrangement.

Oxime rearrangement is initiated by the formation of a N-protonated oxime by the attack of the proton from a Brønsted acid site to the nitrogen atom of oxime, followed by the proton transfer from nitrogen to oxygen atom (Scheme 2) [59,60]. The formation of O-protonated oxime by proton transfer from nitrogen to oxygen is a 1, 2-H-shift reaction with high activation energy and is



Scheme 2. Possible reaction pathway in the liquid-phase Beckmann rearrangement of cyclohexanone oxime.

considered as the rate-determining step in Beckmann rearrangement. In this process, solvents can play an important role in lowering the activation energy by interacting directly with the N-protonated oxime and forming a cyclic transition state. Such a stabilizing interaction between the solvent molecule and the migrating hydrogen in the transition structure would lower the energy barrier of 1, 2-H-shift. Hence solvents with higher dielectric constants may accelerate the 1, 2-H-shift of the N-protonated oxime due to the higher ability to stabilize the transition structure or to reduce the energy barrier of the transition state. Moreover, polar solvents are also more efficient in assisting the migration of OH_2^+ group from nitrogen to carbon atom. This may explain the lower yield of caprolactam in solvents with lower dielectric constants such as chlorobenzene.

This implies that solvents with high dielectric constants such as DMF and DMSO should give higher yields of caprolactam since they can accelerate not only the 1, 2-H-shift but also the subsequent rearrangement. However, the experimental observation is the opposite. Here, we should take into consideration the basicities of the solvents as well. DMF and DMSO possess higher basicity than benzonitrile [61] and hence adsorb more strongly on the catalyst active sites, which essentially means that solvent probably poisons the active acid sites on the catalyst. Hence cyclohexanone oxime molecules are practically prevented from adsorption. When the first step of adsorption of cyclohexanone oxime on catalyst surface itself does not take place, the ability of these solvents to enhance the rates of 1, 2-H-shift and migration of OH_2^+ group (which are subsequent steps) is of no use and the yield of caprolactam is again lower.

Hence, the facility of protonation of oxime through the adsorption of substrate on the active site depends on the competitive adsorption between substrate and solvent. On the other hand, a solvent having a higher dielectric constant or a more polar nature is preferred in the two subsequent steps of 1,2-H-shift and migration of OH_2^+ group. Therefore, the choice of a suitable solvent depends on the balance between these two aspects. The results of our work indicate that benzonitrile is the most suitable solvent (with optimum values of both parameters) among solvents studied for this reaction over Cs-exchanged heteropolyacids under current experimental conditions. The balanced adsorption of benzonitrile on the catalyst surface resulting from its optimum polarity and basicity helps effective desorption of the lactam produced from the acid sites. This minimises the formation of by-products and increases the rate of Beckmann rearrangement. The ability of benzonitrile to react with water is also proposed to contribute towards the efficiency of benzonitrile as solvent [27]. The formation of small amounts of benzamide was observed during the reaction through acid-catalyzed hydrolysis of benzonitrile.

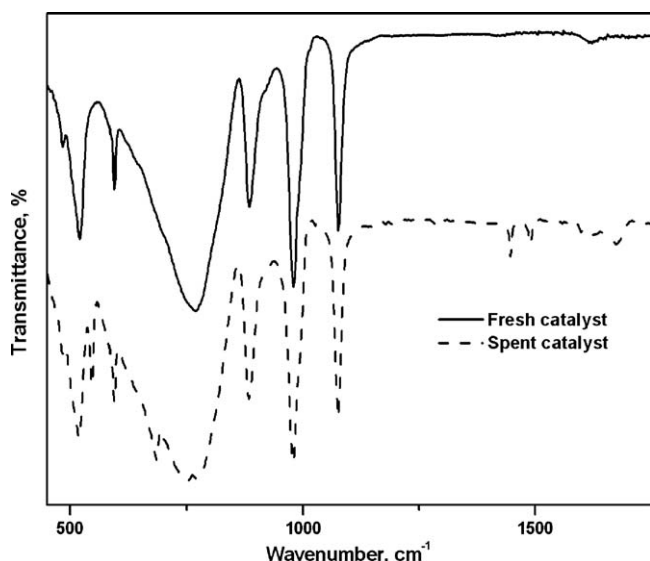


Fig. 7. FTIR spectra of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ before (solid line) and after (dashed line) Beckmann rearrangement reaction of cyclohexanone oxime at 403 K for 45 h. The additional peaks in the spectrum of the spent catalyst are from adsorbed benzonitrile.

trile. Thus, it is likely that the benzonitrile hydrolysis removed any water molecules present in the reaction mixture, which might otherwise have hydrolyzed the oxime, so preventing formation of cyclohexanone.

Note that a different catalyst system and its properties may change the preferred solvent for an efficient rearrangement reaction. Benzonitrile was observed most suitable for rearrangement to ϵ -caprolactam using mesoporous molecular sieves as catalysts previously [27]. However, high selectivities of ϵ -caprolactam was obtained with zeolite beta catalysts in chlorobenzene [22]. An active solvent participation was observed also in case of the rearrangement of 4-hydroxyacetophenone oxime using beta zeolites [58]. Based on the influences of the competitive adsorption between 4-hydroxyacetophenone oxime and a series of solvents with different dielectric constants on the catalytic performance of beta zeolites, it was suggested that facility of protonation of oxime is mainly dependent upon the competitive adsorption between substrate and solvent.

In order to check the stability of the catalyst during reaction, the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyst was reused for the Beckmann rearrangement of cyclohexanone oxime after filtering out the catalyst and washing several times with acetone. The activity and selectivity towards ϵ -caprolactam were comparable to that of fresh $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyst after recycling two times (Table 1). The $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyst used for 45 h of reaction at 403 K was examined by IR spectroscopy (Fig. 7). The spectrum was similar to that of fresh catalyst except the additional bands from adsorbed benzonitrile which shows that the catalyst is structurally stable after the reaction.

4. Conclusions

The Cs salts of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ are investigated for Beckmann rearrangement of oximes to the corresponding amides in heterogeneous liquid-phase system. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is the most selective for the formation of ϵ -caprolactam from cyclohexanone oxime among the Cs salts studied. The high selectivity obtained for the desired product offers very significant advantage over vapor-phase rearrangement of cyclohexanone oxime which requires high temperatures to keep the oxime and products in vapor-phase and to facilitate the desorption of oxime and lactam, resulting in

formation of several byproducts. The nature of the solvent has a strong effect on the activity of the catalyst and benzonitrile is found to be most suitable solvent. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is also highly active and selective for the Beckmann rearrangement of other oximes such as acetophenone, benzophenone and their derivatives to the corresponding amides, and it is possible to achieve good conversion of oximes in relatively short reaction times. In conclusion, our results show that the cesium exchanged tungstophosphoric acid can be effectively used, in the presence of a suitable solvent, for the rearrangement of oximes under relatively mild liquid phase conditions with minimal formation of byproducts.

References

- [1] G. Bellussi, C. Perego, *CATTECH* 4 (2000) 4.
- [2] G. Dahlhoff, J.P.M. Niederer, W.F. Hölderich, *Catal. Rev.* 43 (2001) 381, and references therein.
- [3] H. Ichihashi, M. Ishidab, A. Shigab, M. Kitamura, T. Suzukia, K. Suenobuc, K. Sugitaa, *Catal. Surv. Asia* 7 (2003) 261, and references therein.
- [4] H. Ichihashi, H. Sato, *Appl. Catal. A* 221 (2001) 359.
- [5] P. Botella, A. Corma, S. Iborra, R. Montón, I. Rodríguez, V. Costa, *J. Catal.* 250 (2007) 161.
- [6] L. Forni, G. Fornasari, C. Tosi, F. Trifirò, A. Vaccari, F. Dumeignil, Grimblot J., *Appl. Catal.* 248 (2003) 47.
- [7] L.X. Dai, K. Koyama, M. Miyamoto, T. Tatsumi, *Appl. Catal. A* 189 (1999) 237.
- [8] A.B. Fernández, I. Lezcano-Gonzalez, M. Boronat, T. Blasco, A. Corma, *J. Catal.* 249 (2007) 116.
- [9] B. Bonelli, L. Forni, A. Aloise, J.B. Nagy, G. Fornasari, E. Garrone, A. Gedeon, G. Giordano, F. Trifirò, *Microporous Mesoporous Mater.* 101 (2007) 153.
- [10] D. Shouro, Y. Moriya, T. Nakajima, S. Mishima, *Appl. Catal. A* 198 (2000) 275.
- [11] L. Forni, G. Fornasari, F. Trifirò, A. Aloise, A. Katovic, G. Giordano, J.B. Nagy, *Microporous Mesoporous Mater.* 101 (2007) 168.
- [12] J. Röseler, G. Heitmann, W.F. Hölderich, *Appl. Catal. A* 144 (1996) 319.
- [13] G.P. Heitmann, G. Dahlhoff, W.F. Hölderich, *Appl. Catal. A* 185 (1999) 99.
- [14] G.P. Heitmann, G. Dahlhoff, J.P.M. Niederer, W.F. Hölderich, *J. Catal.* 194 (2000) 122.
- [15] R. Xing, Y. Liu, Y. Wang, L. Chen, H. Wu, Y. Jiang, M. He, P. Wu, *Microporous Mesoporous Mater.* 105 (2007) 41.
- [16] T. Ushikubo, K. Wada, *J. Catal.* 148 (1994) 138.
- [17] T.D. Conesa, J.M. Campelo, D. Luna, J.M. Marinas, A.A. Romero, *Appl. Catal. B* 70 (2007) 567.
- [18] A. Aucejo, M.C. Burguet, A. Corma, V. Fornés, *Appl. Catal.* 22 (1986) 187.
- [19] A. Thangaraj, S. Sivasanker, P. Ratnasamy, *J. Catal.* 137 (1992) 252.
- [20] L.X. Dai, R. Hayasaka, Y. Iwaki, K.A. Koyano, T. Tatsumi, *Chem. Commun.* (1996) 1071.
- [21] A. Corma, H. García, J. Primo, *Zeolites* 11 (1991) 593.
- [22] M.A. Camblor, A. Corma, H. García, V. Semmer-Herléan, S. Valencia, *J. Catal.* 177 (1998) 267.
- [23] S. Sato, K. Urabe, Y. Izumi, *J. Catal.* 102 (1986) 98.
- [24] T. Curtin, J.B. McMonagle, B.K. Hodnett, *Catal. Lett.* 17 (1993) 145.
- [25] H. Sato, K. Hirose, Y. Nakamura, *Chem. Lett.* 22 (1993) 1987.
- [26] P.S. Singh, R. Bandyopadhyay, S.G. Hegde, B.S. Rao, *Appl. Catal.* 136 (1996) 249.
- [27] C. Ngamcharussrivichai, P. Wu, T. Tatsumi, *J. Catal.* 227 (2004) 448.
- [28] C. Ngamcharussrivichai, P. Wu, T. Tatsumi, *J. Catal.* 235 (2005) 139.
- [29] C. Ngamcharussrivichai, P. Wu, T. Tatsumi, *Chem. Lett.* 33 (2004) 1288.
- [30] W.F. Hölderich, *Catal. Today* 62 (2000) 115.
- [31] M.J. Climent, A. Corma, S. Iborra, *J. Catal.* 233 (2005) 308.
- [32] C. Ngamcharussrivichai, P. Wu, T. Tatsumi, *Appl. Catal. A* 288 (2005) 158.
- [33] A.B. Fernández, A. Marinas, T. Blasco, V. Fornés, A. Corma, *J. Catal.* 243 (2006) 270.
- [34] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [35] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171; I.V. Kozhevnikov, *Catalysts for Fine Chemical Synthesis*. Vol. 2. Catalysis by Polyoxometalates, Wiley & Sons, Chichester, UK, 2002, and references therein.
- [36] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199; M. Misono, *Chem. Commun.* 13 (2001) 1141; N. Mizuno, M. Misono, *Chem. Lett.* 16 (1987) 967.
- [37] T. Nishimura, T. Okuhara, M. Misono, *Appl. Catal.* 73 (1991) L7.
- [38] Y. Izumi, M. Ogawa, W. Nohara, K. Urabe, *Chem. Lett.* 21 (1992) 1987.
- [39] T. Okuhara, M. Yamashita, K. Na, M. Misono, *Chem. Lett.* 23 (1994) 1451.
- [40] P. Guyraud, N. Essyem, J.C. Vedrine, *Catal. Lett.* 56 (1999) 35.
- [41] A. Corma, M. Martínez, C. Martínez, *J. Catal.* 164 (1996) 422.
- [42] K. Na, T. Okuhara, M. Misono, *J. Chem. Soc., Faraday Trans. 1* (91) (1995) 367.
- [43] K. Na, T. Iizaki, T. Okuhara, M. Misono, *J. Mol. Catal.* 115 (1997) 449.
- [44] N. Essayem, G. Coudurier, M. Fournier, J.C. Vedrine, *Catal. Lett.* 34 (1995) 223.
- [45] M. Kimura, T. Nakato, T. Okuhara, *Appl. Catal.* 165 (1997) 227.
- [46] T. Okuhara, M. Kimura, T. Nakato, *Chem. Lett.* 26 (1997) 839.
- [47] T. Okuhara, T. Nishimura, H. Watanabe, M. Misono, *J. Mol. Catal.* 74 (1992) 247.
- [48] T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru, M. Misono, *Chem. Mater.* 12 (2000) 2230.
- [49] K. Narasimharao, D.R. Brown, A.F. Lee, A.D. Newman, P.F. Siril, S.J. Tavener, K. Wilson, *J. Catal.* 248 (2007) 226.

- [50] T. Okuhara, *Catal. Today* 73 (2002) 167.
- [51] A.I. Vogel, *Vogel's Text Book of Practical Organic Chemistry*, Fourth edition, Longman, London, 1978.
- [52] P.F. Siril, D.R. Brown, *J. Mol. Catal. A* 252 (2006) 125.
- [53] S.P. Felix, C.S. Jowitt, D.R. Brown, *Thermochim. Acta* 433 (2005) 59.
- [54] J.F. Keggin, *Proc. R. Soc. London A* 144 (1934) 75.
- [55] J.B. McMonagle, J.B. Moffat, *J. Colloid Interface Sci* 101 (1984) 479; J.B. Moffat, J.B. McMonagle, D. Taylor, *Solid State Ionics* 26 (1988) 101.
- [56] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, Fourth ed., Wiley, New York, 1992.
- [57] K.G. Davenport, C.B. Hilton, US Patent 4 524 217 (1985).
- [58] Y.M. Chung, H.K. Rhee, *J. Mol. Catal. A* 159 (2000) 389.
- [59] K. You, L. Mao, D. Yin, P. Liu, H. Luo, *Catal. Commun.* 9 (2008) 1521.
- [60] M.T. Nguyen, G.T. Raspoet, L.G. Vanquickenborne, *J. Am. Chem. Soc.* 119 (1997) 2552.
- [61] W.R. Fawcett, M.A. Brynda, T.G. Smagala, *Russ. J. Electrochem.* 44 (2008) 28.